i								
REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188			
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information.						S searching existing data segures anthonio and		
including suggestions for	ed, and completing and review	ing this collection of information.	Send comments regarding this be	urden estimate or an	s, searching existing v other aspect of this	data sources, gathering and		
I Highway Suite 1204 Adir	oton VA 22202 4202 Boson	adaala ahaala ka aa aa a	-quartois dervices, Directorate i	or miorination Opera	itions and Henorts (0	704-0188) 1215 Jefferson Davis		
collection of information if	it does not display a currently t	nent of Detense, Washington Hea ondents should be aware that notw valid OMB control number. PLEAS	ithstanding any other provision of	of law, no person sha	Il be subject to any p	enalty for failing to comply with a		
1. REPORT DATE	(DD-MM-YYYY)	2. REPORT TYPE	SE DO NOT RETURN TOUR FO	DHM TO THE ABOVE	E AUDRESS.			
Ī	,				3. DATES CO	VERED (From - To)		
4. TITLE AND SUB	**************************************	Technical Papers	er.		i	•		
4. IIILE AND SUB	IIILE				5a. CONTRA	CT NUMBER		
						INDIVIDEN		
						UMPED		
l ·					5b. GRANT N	IUMBER		
						i e		
					5c. PROGRA	M ELEMENT NUMBER		
						1		
6. AUTHOR(S)								
` '					5d. PROJEC	NUMBER		
					2303	1		
						5e. TASK NUMBER		
		•			M 2C8 5f. WORK UN	IT NUMBER		
7. PERFORMING O	RGANIZATION NAME	(S) AND ADDRESS(ES)						
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)						8. PERFORMING ORGANIZATION		
Air Force Posses	h Laboratory (AFM	<b>a</b> /			REPORT	•		
AFDI ODG	11 Lautoratory (AFM	<b>L)</b>						
AFRL/PRS	* **	•	* * *					
5 Pollux Drive				1		• •		
Edwards AFB CA	03524 7049							
Lawards Arb CA	93324-7048				A			
				İ				
9. SPONSORING / I	MONITORING AGENC	Y NAME(S) AND ADDRE	(00/50)					
		I MAINE(S) AND ADDRE	(SS(ES)		10. SPONSOF	/MONITOR'S		
					ACRONYM(S)			
				i	` [			
Air Force Researc	h Laboratory (AFM)	C)			İ			
AFRL/PRS		•		L				
5 Pollux Drive				1	11. SPONSOR/MONITOR'S			
Edwards AFB CA 93524-7048						S)		
Edwards AFB CA	93524-7048				,	`		
40 DIOTRIBUTION								
12. DISTRIBUTION	AVAILABILITY STAT	EMENT		l_				
			•					
					1	,		
Approved for public release; distribution unlimited.								
11 F	re rerease, distribution	on unmined.						
			•		<i>*</i>	l		
13. SUPPLEMENTAL	RY NOTES							
		•						
					-			
14. ABSTRACT	<del></del>							
T. ADSTRACT			the second second					
						į.		
					:	· ·		
					1	1		
					•	I		
			•		:	1		
						Ì		
			•			i		
						!		
						į		
				4 4	ni 🗪	. 1 .		
				11	2/0	71		
			•	- 1	•	1		
·								
15. SUBJECT TERMS	}	· · · · · · · · · · · · · · · · · · ·		· · · · · · · · · · · · · · · · · · ·				
	-			•				
		,						
6. SECURITY CLAS	SIFICATION OF:	······································	17. LIMITATION	10 NUMBER	140			
			OF ABSTRACT	18. NUMBER		OF RESPONSIBLE		
			O ADSTRACT	OF PAGES	PERSON	İ		
. REPORT	h ADOTE LOT		1	1	Leilani R	chardson		
. NEFUNI	b. ABSTRACT	c. THIS PAGE		1		PHONE NUMBER		
			/ A Th	1	(include area			
Unclassified	Unclassified	Unclassified	1 (")		(661) 275			
		<u></u>	<u> </u>	1	1 (001) 213	-2012		

62

servicate Herrs are and

Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std. 239.18

CF

### MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)

30 Apr 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-1998-090

H.Y. Yoo and Jerry Boatz "Theoretical Study of the Mechanism of the Decomposition Process of High Energy Density Materials"

HEDM Conference Presentation (Statement A)

### 20021121 041

## Theoretical Study of the Mechanism of the Decomposition Process of High Energy Density Materials

Hi Young Yoo and Jerry Boatz\*

\*Air Force Research Laboratory, Edwards AFB, CA 93524-7680 National Research Council, Washington, DC 20418

AFOSR HEDM CONTRACTOR'S MEETING 5/18-20, 1998 MONTEREY, CA

**DISTRIBUTION STATEMENT A**Approved for Public Release
Distribution Unlimited

### Theoretical Study of the Mechanism of the Decomposition Process of High Energy Density Materials

Hi Young Yoo and Jerry Boatz

National Research Council, Washington, DC 20418 Air Force Research Laboratory, Edwards AFB, CA 93524-7680

One of the goals of the HEDM program is the development of high performance monopropellants which are also less toxic than currently used systems such as hydrazine. Included in this effort is the characterization of decomposition mechanisms, as an initial step toward identification of a suitable catalyst. *Ab initio* quantum mechanical calculations are performed on the decomposition mechanisms of [NH<sub>2</sub>Me<sub>2</sub>]<sup>†</sup>[NO<sub>3</sub>], a potential monopropellant replacement for hydrazine. The potential energy surfaces of two gas-phase decomposition processes have been explored: (1) proton transfer and (2) methyl cation transfer reactions. These reaction pathways have been examined for both the isolated cation [NH<sub>2</sub>Me<sub>2</sub>]<sup>†</sup> and in the presence of a counter anion, X=Cl, [NO<sub>3</sub>]. For X=Cl, transition states for both pathways have been located at the RHF/6-31G\* level and the corresponding intrinsic reaction coordinates (IRCs) have been traced. Comparison of activation barriers and reaction enthalpies for these gas-phase decomposition pathways will be presented here.

$$[NH_2Me_2]^{\dagger}[X] \rightarrow NHMe_2 + HX \tag{1}$$

$$[NH_2Me_2]^+[X]^- \rightarrow NH_2Me + MeX$$
 (2)

Hydrazine is the state of the art monopropellant currently. However, it has several disadvantages including toxicity, volatility, and handling.

Researchers are continually looking for new monopropellant candidates which include energetic materials such as substituted ammonium salts. Our research effort has concentrated on the decomposition routes of some carried out by our group to explore possible decomposition mechanisms. HEDM materials. Ab initio quantum mechanical calculations have been

The model compounds under study are  $[NH_2Me_2]^+[X]$ , where  $X = NO_3$  and Cl, and  $[N(NH_2)_2Me_2]^+[NO3]$ .

- To map out the potential energy surface of these model compounds
- To determine the energetics of decomposing species
- . To design a catalyst that stabilizes the transition state

### Decomposition Mechanisms of [NH<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>[X]<sup>-</sup>, $X = CI \text{ or } NO_3$

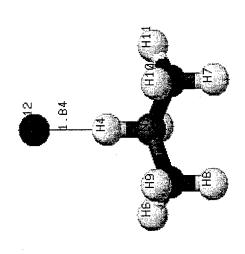
Proton Transfer

$$[NH_2Me_2]^+[X]^- \rightarrow NHMe_2 + HX$$

Methyl Cation Transfer

$$[NH_2Me_2]^+[X]^- \rightarrow NH_2Me + MeX$$

### A Proton Transfer Transition Structure of [NH2Me2]<sup>+</sup>[CI] At RHF/6-31G\*(6d)



1.46 1.39 1.39 1.39 1.39 1.39

Intermediate Complex

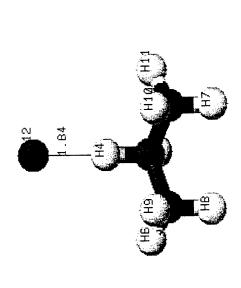
Transition Structure

Energy (kcal/mol)

0.0

4.6

# A Methyl Cation Transfer Transition Structure of [NH<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>[CI]<sup>-</sup> At RHF/6-31G\*(6d)



Transition Structure

(kcal/mol) Energy

Intermediate Complex

# Calculated Reaction Energies of [NH<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>[Cl]

### Proton Transfer

$$[NH_2Me_2]^+[CI]^- \rightarrow NHMe_2 + HCI$$

10.7 kcal/mol

Methyl Cation Transfer

$$[NH_2Me_2]^+[CI]^- \rightarrow NH_2Me + MeCI$$

8.1 kcal/mol

### CONCLUSION

Based on the ab initio calculation studies of [NH2Me2] [CII]

- process is much lower than that of the methyl cation transfer The activation energy of the proton transfer decomposition pathway.
- The transition structure of proton transfer is much tighter than that of methyl cation transfer.
- The methyl cation transfer pathway is 2.6 kcal/mol less endothermic than the proton transfer process.
- Our calculations imply that the proton transfer is most likely the first step to occur in the decomposition process of [NH<sub>2</sub>Me<sub>2</sub>]<sup>†</sup>[CI].